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Ionic Polymerization[1]. Ion Pair Chain Mechanisms. The
Effect of Different Lewis Acid Catalysts on the Monomer
Reactivity Ratios in Copolymerization.

by G. G. Overberger, R. J. Ehrig[2] and David Tanner.

ABSTRACT

With the copolymer system styrene, p-chlorostyrene in
solvent mixtures of carbon tetrachloride and nitrobenzene,
no difference in monomer reactivity ratios were obtained
with aluminum bromide, ferric chloride, titanium tetrachlor-
ide, stannic chloride and titanium tetrachleride-trichloro-
acetic acid as catalysts in homogeneous solution. In these
solvent systems with the above catalysts no measurable frag-
ments from the solvent or catalysts were incorporated in
purified polystyrenes obtained from styrene alone with the
exception of aluminum bromide in pure nitrobenzene as a sol-
vent and antimony pentachloride in a 1:1 carbon tetrachloride
nitrobenzene solution. The insensitivity of monomer reactivity
ratios in this system to changes in dielectric constant and

catalyst concentration previously noted with a stannic chloride catalyst was verified with other catalysts.

In a previous paper, the effect of reaction conditions on the monomer reactivity ratios for the copolymerization of

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1) This is the third in a series of papers concerned with ionic polymerization. For the second paper, see C. G. Overberger, L. H. Arond, D. Tanner, J. J. Taylor and T. Alfrey, Jr., THIS JOURNAL, 74, 4848 (1952). A portion of this work was supported by a contract from the Office of Naval Research.
2) A portion of a thesis submitted by R. J. Ehrig in partial fulfillment of the requirements for the degree of Master of Science to the graduate school of the Polytechnic Institute of Brooklyn.

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styrene and p-chlorostyrene was investigated in order to use this technique to study the mechanism of ion pair addition to the double bond[3]. An important variable which was not includ-

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3) C. G. Overberger, L. H. Arond, J. J. Taylor, THIS JOURNAL, 73, 5541 (1951)

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ed in the previous work is the effect of variation in types of catalyst. Information of this type was sought in order to aid in the elucidation of the mechanism of the propagation step[1]. In addition, it was desirable to determine whether any fragments from the catalysts or solvent remained in the polymer chain after purification. This paper reports the monomer reactivity ratios obtained for the system styrene-p-chlorostyrene in carbon tetrachloride, nitrobenzene mixtures or in pure nitrobenzene for ferric chloride, titanium tetrachloride, titanium tetra-

chloride-trichloroacetic acid and aluminum bromide. Additional data obtained with stannic chloride in pure nitrobenzene and with aluminum bromide in pure carbon tetrachloride are also reported. The anomalous behavior of antimony pentachloride is noted.

EXPERIMENTAL

Solvents and Monomers.

Carbon tetrachloride, nitrobenzene, styrene and p-chlorostyrene were purified as described previously[3].

Catalysts.-

Stannic chloride was purified and ampules prepared according to the procedure described previously[3].

Titanium tetrachloride, C.P., (Eimer and Amend) was purified in the same manner as the stannic chloride except that the titanium tetrachloride was refluxed with a small amount of very fine, pure copper strips to remove the last traces of light color[4] in the titanium tetrachloride. The

4) C. K. Stoddard and E. Pietz, U.S. Bur. Mines, Rept. Invest. 4153, 1947; see C.A. 42, 2406 (1948)

titanium tetrachloride was distilled under nitrogen and ampules were prepared in a nitrogen atmosphere as previously described[3]. The filled ampules were colorless.

Anhydrous ferric chloride, C.P., (Eimer and Amend) was purified by sublimation in an apparatus similar to that described for the preparation of the Lewis acid by B. R. Tarr[5].

A few minor changes were necessary. After the apparatus was

5) B. R. Tarr, "Inorganic Syn.", Vol. III, McGraw-Hill Book
Company, Inc., New York, 1950, p. 191.

flame dried, ferric chloride was quickly put into the reaction

chamber. This entire apparatus was then swept with dry nitro-

gen and again flame dried. If any yellow coloration due to

hydration was detected at this stage, the apparatus was dis-

mantled, redried, and a new sample was prepared. Dry chlorine

gas was then allowed to flow into the system by means of a two

way stopcock. The ferric chloride was sublimed directly into

five tubes which were attached in series to a 20 mm. glass

tube. The system was again swept with dry nitrogen and each

tube was removed separately by means of an oxygen flame. The

crystals had a reddish brown coloration. The weight of ferric

chloride used in the polymerizations was obtained indirectly

by weighing a bottle before and after the ferric chloride was

transferred from a tube.

Since the melting point of aluminum bromide is 97°, an

all-glass, steam jacketed distillation apparatus, similar in

principle to the apparatus used for stann c chloride[3], was

constructed. In this way the solid aluminum bromide could

be purified by distillation and introduced into ampules.

Antimony pentachloride, C.P., (Eimer and Amend) was

first used without purification in exploratory experiments.

Ampules were prepared in a dry box in an atmosphere of nitro-

gen. The same procedure of filling the ampules was employed

here as for the titanium tetrachloride, except that the
material was not distilled. In some experiments the compound
was distilled but no effect on copolymer composition was de-
tected, b.p. 72°/16 mm. (68°/14 mm.)[6].

6) N. V. Sidgwick, "Chemical Elements and Their Compounds",
    Vol. I, Oxford University Press, Oxford, 1950, p. 794.

Trichloroacetic acid was distilled under reduced press-
ure and ampules were made using the method employed for the
catalyst ampules. It was necessary, however, to keep the en-
tire apparatus warm to prevent crystallization before the
ampules were filled. Five batches of ampules were prepared
and melting points of the samples were taken. The five melt-
ing points had a range of 58-59°(59.4°)[7].

7) J. Kendall and P. M. Gross, THIS JOURNAL, 43, 1426 (1921).

Polymerization Technique.-

The polymerization technique used throughout was that de-
scribed by reference 3, except for modifications employed with
the use of a dry box. The copolymerizations are now carried
out in an air tight, sheet metal dry box equipped with a glass
window and rubber glove fittings. About 24 hours before each
experiment the dry box containing a calcium chloride dish is
flushed with dry nitrogen. Monomers and solvents are intro-
duced into the reaction bottles through the manipulation of
semi-micro and automatic burets respectively which are contain-
ed within the box. In this way it is possible to maintain a
constant, reproducible atmosphere for each run.

Where cocatalysts were employed, the ampules were broken
and the acid dissolved in the solution before the catalyst
was added. In all experiments except those with antimony
pentachloride and aluminum bromide in 1:1 carbon tetrachlor-
ide-nitrobenzene, the reaction was very fast. Due to the high
dielectric constant of the medium employed, the reaction had
to be stopped as soon as the catalyst was injected into the
monomeric solution. The approximate time of most reactions
was between five and ten seconds except those noted. This
was the length of time required to remove the syringe from
the bottle after adding catalyst, unscrew the cap of the
polymerization bottle, and pour the solution into methanol.

All of the catalyst ampules were broken up by violent
shaking and dissolved completely in the solvent mixture with
the exception of aluminum bromide in carbon tetrachloride
which remained as a partial solution.

On injecting aluminum bromide into the monomer mixture
with pure carbon tetrachloride solvent, in a very short time
the color turned from colorless to light orange to dark
orange to red, ... the solution rapidly became warmer as the
color darkened until boiling was noted. By precipitating the
copolymer instantly after injection of aluminum bromide before
any color change, it was possible to avoid any color change
and heat effect.

Percent conversions were calculated from the weight of
polymer obtained. The following formula was used in correct-

ing M_2 for conversions above 6%.

$$M_2 = M'_2 + \frac{M'_2 - m_2}{2} \times conversion$$

where M_2 and M'_2 are the corrected and uncorrected values,
respectively, for the mole fraction of monomer 2 in the monomer
mixture and m_2 is the mole fraction of monomer 2 in the polymer.

RESULTS AND DISCUSSION

Monomer Reactivity Ratios.-

The monomer reactivity ratios obtained in the system
styrene, p-chlorostyrene in the various solvent systems em-
ployed are given in Table I. The experimental data are summar-
ized in Table II. With all catalysts, preliminary experiments
were carried out at 25-75 p-chlorostyrene-styrene ratios in
order to obtain information as to reproducibility and an
estimation of the rate. Most of these data are omitted for
brevity but a representative group of experiments is summariz-
ed in Table III. As can be seen, good duplication of copoly-
mer composition was obtained at low conversions. Typical co-
polymer composition curves are given in Fig. I. Since most
of the copolymer composition curves are similar, they are
omitted for brevity. The heterogeneous aluminum bromide
system in carbon tetrachloride alone gave a small deviation
and is represented in Fig. I. From Table I it can be seen
that in all the homogeneous systems studied, the variation
in the monomer reactivity ratios is small and within the range

of experimental error. The addition of trichloroacetic acid
to titanium tetrachloride as a cocatalyst did not materially
change the monomer reactivity ratios. This system has been
studied by Plesch[8] who has shown the cocatalyst activity of

8) P. Plesch, J. Chem. Soc., 543 (1950).

trichloroacetic acid with titanium tetrachloride. Thus it
seems certain that in solvents of the range of dielectric con-
stant employed here, the different anions from the catalyst-
cocatalyst fragment does not appear to influence the ratios of
the rates of addition of the ion pairs to the double bonds of the
monomers in homogeneous solution.

Florin[9] had reported that different Lewis acid catalysts

9) R. E. Florin, THIS JOURNAL, 71, 1867 (1949); ibid, 73, 4468 (1951).

for the system styrene, 3,4-dichlorostyrene in carbon tetra-
chloride affected the reactivity ratios markedly and explained
his results with the mechanism proposed for cationic catalyzed
polymerization reported by Fontana and Kidder[10] for propylene
in propane at low temperatures with an aluminum bromide-hydrogen
bromide catalyst system. However, with the exception of stannic

10) C. M. Fontana and G. A. Kidder, ibid, 70, 3745 (1948).

chloride, his reported polymerizations were heterogeneous and
his variations may be due to catalytic surface effects. It
is entirely possible, however, that his system did show some
variation due to the greater difference in reactivity between
monomers of his pair.

It is again noted[3] that variation in dielectric constant

from about 2.8 to 30 with a stannic chloride catalyst,
Table I, footnote c, does not affect the monomer reactivity
ratios. Values obtained in nitrobenzene are reported here.
Likewise with titanium tetrachloride and aluminum bromide
as catalysts, no variation in r_1 and r_2 is noted on change
of dielectric constant in this system (Table I). Previously[2],
it had been demonstrated that a change in concentration of
stannic chloride from 0.5 to 2 mol percent in the system p-
chlorostyrene- $\measuredangle$-methylstyrene in carbon tetrachloride did
not result in any change in copolymer composition. In Table
II, data are presented to show that variation in titanium
tetrachloride concentration from 1 to 3 mol percent in the
styrene-p-chlorostyrene system in a 1:1 carbon tetrachloride-
nitrobenzene solution gave no variation in copolymer compos-
ition.

The reactivity ratios and their probable errors were ob-
tained by the use of a previously described procedure[11].

11) a. T. Alfrey,A. Goldberg and W.P.Hohenstein,Ibid,68,2464
(1946).
b. "Copolymerization" by T.Alfrey, J.J.Bohrer and H.
Mark,Interscience Publishers,Inc., New York, 1952.

Catalyst or Solvent Fragments.-

Control experiments using only polystyrene were carefully
precipitated and purified. In no experiment with any of the
solvent systems described in Table I, with ferric chloride,
titanium tetrachloride, titanium tetrachloride-trichloroacetic
acid and stannic chloride were any traces of chlorine or nitro-

gen detected in the polymers either by gravimetric analysis

or infrared analysis[12]. The infrared spectra were not entirely

12) We are grateful to Mr. Gerard Endres, one of our group,
for infrared data on many samples of polystyrene prepar-
ed with stannic chloride as a catalyst.

satisfactory as negative evidence; however, coupled with the

gravimetric results they indicated the absence of any measur-

able solvent or catalyst fragments in the polymer. Usually

from 3 to 5 control polymers were subjected to rigorous purifi-

cation and scrutiny[13].

13) The method of chlorine analysis employed by Dr. Ritter
is described by Pregyl and Roth,"Quantitative Organische
Mikroanalyse", Springer, 5th Edition, page 118. A sample
of pure p-chlorostyrene gave a chlorine value of 25.40%;
calcd. 25.58%. A sample of polystyrene prepared by
catalysis with 2,2-azo-bis-isobutyronitrile in carbon
tetrachloride gave values for chlorine of 0.52% and 0.45%
showing good reproducibility with small quantities of chlor-
ine present. Samples of polystyrenes prepared in bulk with
benzoyl peroxide show the absence of any chlorine by this
procedure as did all control experiments reported here with
ionic catalysis. In this work alone we have had 24 analyses
carried out in duplicate with surprisingly little variation.
Dr. Ritter has informed us that he considers the method to
have a range of accuracy of ± 0.2 ± 0.3%on these polymers.
Larger samples are employed with these polymers than is
usual for increased accuracy.

Thus, the copolymer compositions determined are not sub-

ject to errors due to incorporation of catalyst or solvent frag-

ments. It is always possible that some termination may occur

from the anionic cocatalyst fragment containing the metal by

formation of an organo metallic bond which is hydrolyzed by

precipitation with the polar solvent but this is unlikely.

Number average molecular weights and kinetic evidence obtain-

ed in this laboratory further substantiate this conclusion.

Plesch has reported that the trichloroacetic acid fragment
is found in the polymer when isobutylene is polymerized
in hexane solution at -70° with a titanium tetrachloride-
trichloroacetic acid catalyst (his polymers were precipitat-
ed in hexane and ethyl alcohol as solvents).

The behavior of antimony pentachloride is interesting.
Here chlorine is introduced into the polymer in a 1:1 carbon
tetrachloride-nitrobenzene solution confirming an earlier
observation of Williams[14] who found that antimony pentachlor-

14) G. Williams, J. Chem. Soc., 775 (1940).

ide when used as a catalyst for the polymerization of styrene
in carbon tetrachloride appeared to act as a chlorinating
agent. Determination of the monomer reactivity ratios for
the styrene p-chlorostyrene system with antimony pentachlor-
ide in the solvent system indicated gave values of r_1, 1.7 ±
0.2; r_2, 0.55 ± 0.05 as a result of additional chlorine be-
ing added to the polymer.

Colclough[15] has reported that no catalyst fragment con-
taining antimony remains attached to the polymer chain when

15) R. O. Colclough, J. Polymer Sci., 5, 467 (1952)

styrene is polymerised in nitrobenzene with radioactive
antimony contained in an antimony pentachloride catalyst.
Landler[16] likewise has demonstrated that polystyrene prepared

16) Y. Landler, Rec. trav. chem. 68, 992 (1949).

in nitrobenzene solution with radioactive stannic bromide
contains no bromine or radioactivity.

Preliminary experiments with silver nitrate in benzene-
alcohol solutions with polystyrene, a copolymer of styrene
and p-chlorostyrene, and the polymers prepared with an
antimony pentachloride catalyst indicate that the aliphatic
chloride structure is present.

Acknowledgment

Brooklyn, N.Y.

TABLE I

Effect of Variant Catalysts on Monomer Reactivity Ratios[a]

Catalyst[b]	Reaction Medium	r_1	r_2
$SnCl_4$[c]	nitrobenzene	2.2 ± 0.2	0.45 ± 0.02
$TiCl_4$	nitrobenzene	2.2 ± 0.2	0.45 ± 0.02
$AlBr_3$	nitrobenzene	2.3 ± 0.4	0.36 ± 0.05
$TiCl_4$	nitrobenzene-carbon tetrachloride(1:1)	2.2 ± 0.2	0.45 ± 0.02
$AlBr_3$	nitrobenzene-carbon tetrachloride(1:1)	2.0 ± 0.2	0.34 ± 0.05
$SbCl_5$	"	1.7 ± 0.2	0.55 ± 0.05
$FeCl_3$	nitrobenzene-carbon tetrachloride(1:4)	2.0 ± 0.1	0.43 ± 0.03
$TiCl_4$-CCl_3COOH[c]	nitrobenzene-carbon tetrachloride	2.0 ± 0.4	0.50 ± 0.05
$AlBr_3$	carbon tetrachloride	1.51 ± 0.05	0.40 ± 0.02

a) All experiments carried out with styrene (M_1) and p-chloro-styrene (M_2) monomer mixtures. b) Concentration of catalysts was 1% based on monomers. c) Previously reported results[3] in 50-50 carbon tetrachloride-nitrobenzene mixture; 0.5% stannic chloride based on monomers r_1=2.10 $\pm$ 0.2; r_2=0.35 $\pm$ 0.02; in pure carbon tetrachloride as solvent; 2% stannic chloride based on monomers; r_1=2.5 $\pm$ 0.4; r_2=0.30 $\pm$ 0.03. d) 1%- 0.5% catalyst-cocatalyst concentration respectively, based on monomers.

TABLE II

Copolymerization of Styrene (M_1) with p-Chlorostyrene (M_2) with
Different Lewis Acids[a]

M_2 in monomer mixture[c]	Conversion %	Cl, %[d]	m_2
	Stannic Chloride[b]		
0.243	7	4.30	0.132
.395	3	7.31	.232
.497	3	9.47	.307
.600	2	12.21	.408
.693	1	14.48	.496
.799	13	18.37	.657
	Titanium Tetrachloride[b]		
.506	16	10.50	.345
.613	14	12.84	.432
.694	9	14.83	.510
.791	9	18.18	.654
.252	20	4.63	.143
.427	34	8.30	.266
.517	36	10.66	.351
	Aluminum Bromide[b]		
0.201	8	2.79	0.085
.250	16	4.71	.140
.408	36	8.37	.268
.431	39	7.56	.240
.515	36	9.48	.308
.526	37	9.38	.302
.652	28	12.84	.431
.658	24	13.25	.447
.699	16	14.73	.505
.700	20	15.85	.550
.797	10	15.65	.545
.800	20	18.65	.670

TABLE II (continued)

M_2 in monomer mixture[c]	Conversion %	Cl,%[d]	m_2
Titanium Tetrachloride[e]			
0.218	25	2.64	0.080
.323	12	5.91	.185
.455	8	8.52	.274
.530	16	10.72	.351
.622	6	11.63	.385
.715	6	15.31	.532
.820	8	17.87	.638
.906	4	21.51	.805
.702[f]	11	15.16	.526
.791[f]	7	17.09	.605
Aluminum Bromide[e]			
0.207	10	3.85	0.118
.257	13	4.66	.143
.407	10	7.64	.244
.500	9	9.93	.323
.628	8	12.99	.433
.698	7	14.55	.498
.796	6	17.18	.605
Ferric Chloride[g]			
0.205	13	4.02	0.123
.323	11	5.98	.188
.393	11	7.02	.222
.493	6	9.97	.326
.602	5	12.65	.424
.677	5	14.82	.513
.793	4	17.10	.607
.896	4	20.88	.776
Titanium Tetrachloride-Trichloroacetic Acid[h]			
0.244	5	4.15	0.128
.398	5	7.63	.243
.503	7	10.58	.349
.594	4	13.08	.444
.698	8	16.02	.563
.796	4	17.80	.636

TABLE II (Continued)

M_2 in monomer mixture[c]	Conversion %	Cl, %[d]	m_2
	Aluminum Bromide[i]		
0.199	14	4.38	0.134
.246	16	5.45	.169
.401	10	8.68	.278
.500	12	10.94	.358
.634	9	13.94	.474
.697	10	15.53	.535
.798	9	18.41	.658

a) All experiments carried out at 0°C. b) In pure nitrobenzene as solvent; 1.0% catalyst concentration based on monomers. c) Corrected for finite conversions. d) Analyses by Dr. K. Ritter, Zurich, Switzerland. e) In a 1:1 carbon tetrachloride-nitrobenzene mixture as a solvent; 1.0% catalyst concentration based on monomers. f) In a 1:1 carbon tetrachloride-nitrobenzene mixture as a solvent; 3.0% catalyst concentration based on monomers. g) In a 1:4 nitrobenzene-carbon tetrachloride mixture as a solvent; 1.0% catalyst concentration based on monomers. h) In a 1:4 nitrobenzene-carbon tetrachloride mixture as a solvent; 1.0%, 0.5% catalyst-cocatalyst concentration respectively, based on monomers. i) In pure carbon tetrachloride as solvent; 1% catalyst concentration based on monomers.
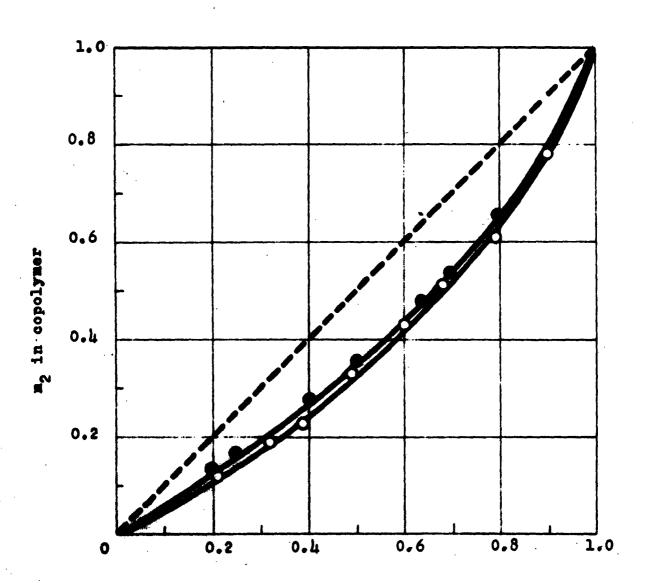
TABLE III

Reproducibility of Copolymerization Experiments[1]. Styrene (M_1) 75 mole%; p-Chlorostyrene (M_2), 25 mole%

Solvent	Catalyst	%Conversion	%Chlorine[4]	m_2, mole%
ϕNO_2	$SnCl_4$	18	4.91	0.15
ϕNO_2	$AlBr_3$	16	4.71	.15
$\phi NO_2/CCl_4$[2]	$SnCl_4$	12	4.46	.14
$\phi NO_2/CCl_4$	$AlBr_3$	13	4.66	.14
CCl_4	$SnCl_4$	14	4.13	.13
CCl_4[3]	$AlBr_3$	16	5.45	.17

1) Similar data were obtained for the other catalyst systems;

2) A 1:1 solution; 3) Heterogeneous solution; 4) Analyses by Dr. K. Ritter, Zurich, Switzerland.

Fig. 1. Copolymerization of styrene (M_1) with p-chlorostyrene (M_2); O, 1% ferric chloride in 1:4 nitrobenzene-carbon tetrachloride. ●, 1% aluminum bromide in carbon tetrachloride.